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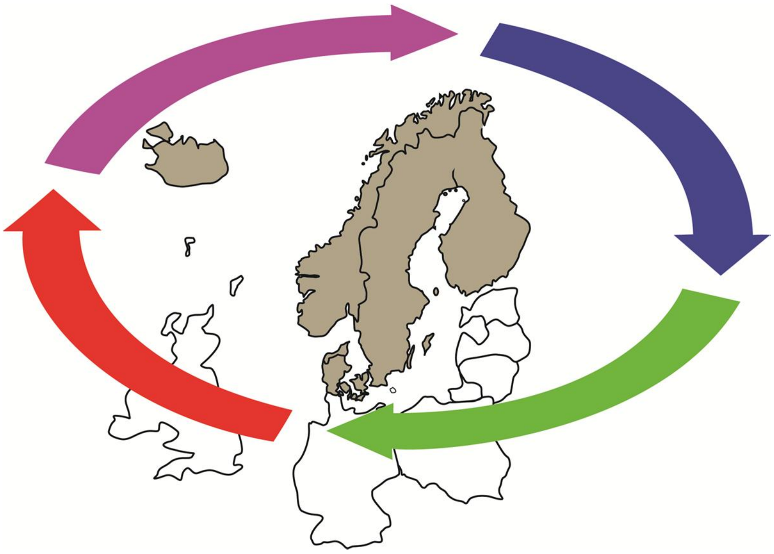

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PART II: ABSTRACTS OF WORK-IN-PROGRESS PAPERS

ENVIRONMENTAL RISK ASSESSMENT OF MOST TRANSPORTED CHEMICALS IN SEA AND ON LAND

– AN ANALYSIS OF SOUTHERN FINLAND AND THE BALTIC SEA

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ABSTRACT

Purpose of this paper

The objective of the study was to assess the risks of the regionally most transported chemicals (oil and petroleum fuels excluded) with a simple scoring system and to highlight the chemicals that require special attention from an environmental point of view in potential railway/road or marine accident situations in the Baltic Sea area. Further, past chemical accidents were compared to study their probability and damages by transport mode and phase.

Design/methodology/approach

Transport volumes of chemicals in Southern Finland and in the Baltic Sea and the overall risk of chemical accidents were surveyed using databases and literature. Altogether 30 chemicals that are transported in high volumes in Southern Finland were assessed from environmental point of view with the scoring method developed especially for accidental situations.

Findings

In case of maritime spills, nonylphenol is the most toxic and hazardous of the studied chemicals. Other very hazardous substances in the case of maritime spills were sulphuric acid and ammonia. Also in the case of an on-land accident, nonylphenol was ranked the most hazardous chemical in soil. The next most hazardous chemicals on the land side are phenol, ammonia and sulphuric acid.

Research limitations/implications
The preliminary results of maritime transportation volumes of chemicals and priority list for environmentally most hazardous chemicals are presented in the study.

Practical implications
The awareness of potential risks of the most transported chemicals is the key factor in increasing the preparedness for and mitigating the effects of possible accidents.

Originality/value
The risk assessment and the chemical priority list compiled in this study could help authorities to pay special attention to the environmentally most hazardous chemicals and to prevent the chemical accident risks in the Baltic Sea area.

Keywords: Chemical transport, Environmental risk management, Scoring method, Transport-related accidents, Logistics.

1. INTRODUCTION

The Baltic Sea is one of the busiest sea routes in the world and it is highly sensitive to the environmental impacts of a possible chemical accident. At present, 25% of the vessels in the Baltic Sea are oil tankers or tankers carrying chemicals. Navigation in the Baltic Sea is challenging due to the relative shallowness, narrow navigation routes, and ice cover of the Baltic Sea. Recently, both the number and the volume of the transported chemicals have increased significantly in the Baltic Sea (HELCOM, 2009), concomitantly raising the spill/ship collision risk in the Baltic Sea areas. The results of previous studies (Rytkönen and Hänninen, 2006; Mullai, 2007; Suominen and Suhonen 2007; EMSA, 2010) indicate that both the spill risks and incidents are less well defined than those for oils, but among the wide range of chemicals transported the potency to cause environmental damage is not negligible. Maritime accidents are fortunately rare, but if they happen the impact on the environment can be considerably high.

High volumes of chemicals are also transported on road and railway in the Southern Finland. Finland has a special location on the edge of EU and the high volumes of Russian transit traffic create a constant risk of accidents. In the event of an accident, hazardous materials can be released to the environment, thereby impacting soil and groundwater, leading to costly emergency response and cleanup efforts. When measuring the impacts of accidents, focus is usually on fatalities/injuries, property damage, and emergency impacts, but exclude environmental and ecological impact associated with releases into soil, groundwater, aquatic features, or natural habitats. Consequently, risk management decisions are being made in the absence of the comprehensive information necessary to mitigate long-term environmental risk (Lewis and Zigi, 2010). Awareness of the potential risks of the most transported chemicals is the key factor for possible accidents.

The first step in risk assessment is the prioritization of chemicals based on their hazards and properties (Singh *et al.*, 2011). The risk depends on both these characteristics and their use pattern, which determines the exposure of the chemicals. Therefore a frequently used substance with relatively low toxicity can still pose a risk to human health and the environment. In many scoring systems, exposure is scored e.g. based on the total volume of the use of the chemical, on the amount of the chemical in a specific industry process or on accidental history the substance has (Singh *et al.,* 2010; Adu *et al.*, 2008). Several indices that combine the chemical hazard and the extent of exposure into one numerical indicator to rank the risk posed by chemicals, have been developed. Davis *et al*. (1994) introduced 51 different chemical ranking systems, and recently many excellent reviews have been published e.g.

Singh *et al*. (2011) and Adu *et al*. (2008). For example, in case of maritime transport, harmful substances in packed form are classified according to IMDG (The International Maritime Dangerous Goods) code into 9 main classes some of which are further divided into subclasses. The classification is the same also in road (ADR) and rail (RID) transportations as the systems have been harmonised by GHS (Globally Harmonised System of Classification and Labelling of Chemicals) of the United Nations (UN). MARPOL 73/78 is an international convection for prevention of pollution of marine environments by ships. The Annex II of the MARPOL contract (regulations for the control of pollution by noxious liquid substances in bulk) introduces a categorisation system for noxious and liquid substances. According to IMO, the four classes used in maritime transportation are category X (major hazard), category Y (hazard), category Z (minor hazard) and other substances (Luhtala, 2010). Even though many classification and assessment method of chemical risks exist, these are equally concentrated on human health effects or methods are focused for evaluation of the effects of long-term chemical exposure (for example pollution from the factory) and not for sudden spill.

The purpose of the study was to assess the risks of the regionally most transported chemicals with a scoring system and highlight the chemicals that require special attention from an environmental point of view in potential on land or in marine accident situations in Southern Finland and in the Finnish coastal areas of the Baltic Sea. The purpose was to evaluate the chemical transportation risk in whole chemical supply chain and that is why scoring was made for both soil and water environment. The chemicals examined in this study were chosen on the basis of transport volumes and known environmental hazardousness of the chemicals. Further, the regularities of the past chemical-related accident were reviewed to show the overall importance of this kind of environmental assessment.

2. METHODOLOGY

The study was conducted in three stages. *In the first stage of the study*, transport volumes of chemicals in Southern Finland and in the Baltic Sea were surveyed. Most of the facts about the transport volumes of chemicals in the Baltic Sea presented in this study have been based on secondary written sources of both Scandinavian, Russian, Baltic and international origin. Furthermore, statistical sources, academic journals, periodicals, newspapers and in later years also different homepages on the Internet have been used as sources of information. In the case of Finland, more specific statistics about chemical transports could be recovered directly from a nationwide vessel traffic system called PortNet. The transport volumes (export and import all together) of bulk chemicals handled in Finnish ports in the years 2008 and 2010 were collected on the basis of dangerous goods declarations gathered from the PortNet system.

In the second stage of the study, a large literature (mainly scientific papers and reports) and database survey about past chemical accidents was made. Worldwide chemical accident databases were reviewed and the most qualified databases were chosen in further examination. In the case of Baltic Sea area, there does not exist any comprehensive chemical accident databases even though some literature about past accidents exists. The best quality chemical accident database called HMIS was found in the US, as some other studies have also shown (e.g. Häkkinen *et al.*, 2010; Mullai, 2007). Therefore, HMIS database was used as the main source in this stage of the study. However, the same regularities related to chemical accidents seem to be valid worldwide based on other database and literature.

In the third stage of the study, altogether 30 chemicals that are transported in Finland and in the Baltic Sea were assessed using the scoring method developed originally by Häkkinen *et* *al*. (2010), though slightly modified for the purpose of this paper. The scoring method was especially developed for chemical accidental situations from environmental point of view. The chemicals for the study were chosen according to the PortNet analysis (section 3.1). From the chemicals studied in this paper, 13 can be classified as very high volume chemicals. The rest of the chemicals have lower transport volumes, and they were chosen for the study on the grounds of pre-evaluations regarding their environmental properties. The chemicals were scored from 0 to 3 according to factors affecting their environmental fate or mobility, ecotoxicology and probability for accident (Table 1). The priority list was formed by calculating together all the given points. Scoring was made separately for soil and water environment. Scored parameters were partly the same in both cases, but the parameters affecting the mobility of chemicals differ at some extent between soil and sea. Parameter values for chemicals were gathered from scientific articles, from the EU, Canada and United States Environmental Agency risk assessment reports, from field literature and from databases. Data gaps were filled by modeling using the US EPA EPISuite program. The EPISuite has been used worldwide in several scoring methods to fill in data gaps (e.g. Juraske *et al*. 2007). The environmental fate and the ecotoxicology values used in the scoring and their references have been complied in Häkkinen *et al*. (2010) for most chemicals and are not presented in this paper. For NExBTL and ETBE, the parameter values were gathered from the ECHA (2012) database and California Environmental Protection Agency (2010).

Scored parameters

In the case of sudden chemical spill to soil, chemicals can migrate into soil as own non-aqueous phase liquids (NAPL). Mobility in environmental media was determined using ***the density to viscosity ratio***. NAPLs migrate vertically downward in soil under the force of gravity and a high density to viscosity ratio of NAPL corresponds to greater potential mobility (Newell *et al*., 1995) leading greater risk of groundwater contamination in accident situation. If the density to viscosity ratio is higher than 0.3 kg/l/cP, the time to reach groundwater in dry sand can be calculated to be less than one day according to Darcy´s law. If the ratio is under 0.01, it takes over one month for NAPL to reach the groundwater. Water has a density to viscosity ratio of 1. The density to viscosity ratio does not significantly affect the transport potential of solid chemicals because they transfer into the environment mainly dissolved in water. In addition to the density to viscosity ratio, the adsorption potential according to ***the organic carbon-water partitioning coefficient (K_{OC})*** was used for assessing the chemical transport in soil. K_{OC} is one of the most important parameters for depicting the transfer and fate of organic contaminants in a soil-water system. Higher K_{OC} values correlate to less mobile chemicals while lower K_{OC} values correlate to more mobile chemicals.

In the maritime case, three major physical-chemical characteristics, including density, water solubility and vapour pressure, determine the fate of the chemical (French McKay *et al*., 2006). ***The water solubility*** is the most important parameter when assessing the chemicals hazard potential for the water environment and biota. In the scoring method the most water soluble chemicals were considered most likely to transport and, therefore, the most hazardous. Most of the studied chemicals are very water soluble. ***The density*** determines the buoyancy relative to water. The chemical quickly disperses if its water solubility is high but it floats or sinks depending on the chemical´s density if its solubility is lower. Since in this study the ecotoxicological effect on water column biota was weighted, the chemicals that sink (density > 1.025 g/cm^3) got 2 points while floaters got 1 point (density < 1.025 g/cm^3) (GESAMP, 2002; French McKay *et al*., 2006). Many risk scenarios have an opposite view, especially when prioritizing public health.

The volatility, persistence in the environment, accumulation and ecotoxicity were estimated in the same way in both soil and marine environment. ***The volatility*** of the chemicals was assessed according to vapour pressure. The largest value was given to compounds with poor volatility (low vapour pressure), since a larger portion of these chemicals stay in the water column or percolate into the soil and transfer into ground water. In this study, the effect of studied chemicals on water or soil biota was weighted and therefore environmental impact risk of non-volatile chemicals is higher. ***Biodegradability*** of chemicals was defined with the BIOWIN3-values which were modelled with the US EPA´s EPISuite program. Modelled values were used to harmonize half-life values. Based on the BIOWIN3-values, chloroform and benzene are the most persistent of the studied chemicals, thus having the highest long-term risk to the environment. For the most part, the modelled values correlate well to experimental values found in scientific literature excluding, inorganic compounds. However, for example chloroform (classified as persistent) degrades anaerobically quite fast, even though its aerobic degradation is relatively slow. Furthermore, the half-life of benzene (classified as persistent) varied between 0.2–679 days in several microcosm studies depending on the conditions (Aronson et al. 1998). Abiotic factors contribute especially to the persistence of TDI, and this was taken into consideration in the scoring system (Table 1 & 4). TDI readily degrades by hydrolysis and the half-life of TDI in water is less than 1 minute (Yakabe *et al*., 1999).

The accumulation of chemicals was estimated using the octanol-water partition coefficient (K_{OW}). The greater the K_{OW}, the more hydrophobic and bioaccumulative the chemical is. The majority of the chemicals studied are not accumulative ($\log K_{OW} < 3$) and they can be considered relatively non-hazardous to the environment. From the chemicals studied only 1-decene and nonylphenol are highly accumulative. ***The acute and chronic toxicity*** of chemicals was examined on three trophic levels (algae, *Daphnia magna* – water flea and fish) according to the lowest defined acute LC/EC50 and chronic NOEC values. Water toxicity values were used also in soil risk assessment because toxicity values for soil organisms could not be found for most chemicals. The averages of the toxicity scoring points from the fish, water flea and algae were calculated individually for acute and chronic toxicity. The most toxic chemicals in this study are nonylphenol and ammonia while the least toxic are ethanol, MTBE and NexBTL. The difference in species sensitivity is the most obvious in bronopol which is clearly more acutely and chronically toxic to algae than to other species.

In addition to the aforementioned factors, several others affect the environmental hazard of chemicals. These ***other hazardous effects*** include smell and taste defects of ground water, carcinogenicity and significantly hazardous degradation and metabolic compounds. These factors were taken into consideration in the scoring even though the comparison of different factors is challenging. Some chemicals were given 0.5–1 additional points for characteristics that are directly hazardous to the environment or health. This scoring was based on the writers own expert judgment and on the information gathered from literature. For example, chemicals that are classified as carcinogenic or likely to be carcinogenic according to the international cancer organization IARC were given 0.5 additional points. A whole additional point was given to the chemicals that were considered to have properties that are of significance in transport accident situations and from an environmental point of view. Nonylphenol is a typical endocrine disrupter and MTBE causes taste and smell defects in ground water in considerably lower concentrations than in which reported toxic effects occur. Ammonia vaporizes quickly into a toxic gas cloud in accident situations and, additionally, the indirect effects on the ecosystem level cause the eutrophication of water bodies, changes in pH and, as a consequence, changes in species composition. Only local effects were considered when assessing environmental risk because a single leakage accident is very rarely significant on a global scale. The basis for the extra points is presented in more detail in Häkkinen *et al.* (2010).

The chemicals that are transported the most inflict the greatest risk for accidents. Sea ***transport volumes*** of chemicals collected in the PortNet system can be considered more reliable than road transport volumes of chemicals and, therefore, the PortNet data is used in environmental risk assessments of various chemicals presented in this paper.

Table 1. Parameters and threshold levels for the scoring used in risk assessment.

Parameter	1 point	2 points	3 points
Volatility (Vapor pressure)[a*]	> 0,1 kPa highly volatile	10^{-5}–0,1 kPa semi-volatile	<10^{-5} kPa non-volatile
Density to viscosity ratio (Soil only)[b]	<0,01kg/l/cP	0,01–0,3 kg/l/cP	>0,3 kg/l/cP
Density (Sea only)	< 1,025 g/cm^3 floater	> 1,025 g/cm^3 sinker	
Adsorbtion (K_{OC}) (Soil only)[a]	>2000 non-mobile	150–2000 slightly/moderately mobile	<150 very mobile/mobile
Water solubility[a]	0,1–10 mg/L poorly soluble	10–1000 mg/L soluble	> 1000 mg/L very soluble
Persistence (BIOWIN3 half life)	Days to weeks	Weeks	Weeks to months
Bioaccumulation (logK_{OW})[a]	<3 not accumulative	3–5 slightly/moderate accumulative	>5 very accumulative
Acute toxicity (LC/EC50)[a]	> 100 mg/L slightly toxic	1–100 mg/L toxic/hazardous	< 1mg/L very toxic
Chronic toxicity (NOEC)[a]	> 1mg/L very slightly toxic	0,1–1,0 mg/L slightly toxic	< 0,1 mg/L very toxic
Other environmental or health effect	0.5–1 extra points for chemicals having other hazardous properties to environment or health		
Transportation volume	<10 000 tonnes	10,000–100,000 tonnes	>100 000 tonnes

[a]The threshold values from Nikunen and Leinonen (2002) were used as guidance in classification. * At sea scenario volatility threshold values determined according to French McKay *et al.* (2006).

[b]For ammonia only 2 points were given, since it becomes a gas at normal temperature. For resorcinol (solid) 0 points.

[c]For TDI only 1 points were given due to degradation by hydrolysis. Creosote and NExBTL has not BIOWIN value, but 3 points were given for creosote and 1 point for NexBTL according to experimental half-lifes from literature.

3. RESULTS AND DISCUSSION

3.1. Transport volumes of chemicals in the Baltic Sea and in Finland

The study revealed that every year more than 11 million tonnes of liquid bulk chemicals are handled in the Baltic Sea ports. The liquid bulk chemicals accounts for approximately 4 % of the total amount of liquid bulk cargoes handled in the Baltic Sea ports. Over half of all the liquid bulk chemicals in the Baltic Sea ports are handled in Finnish and Swedish ports. The most handled chemicals in the Baltic Sea ports area are methanol, sodium hydroxide solution, ammonia, sulphuric and phosphoric acid, pentanes, xylenes, methyl tert-butyl ether (MTBE) and ethanol and ethanol solutions. All of these are transported at least several hundred thousand tonnes per year. Further, high amounts of liquid fertilisers, such as solution of urea and ammonium nitrate in water, are handled in the Baltic Sea ports (Posti and Häkkinen, 2012).

The PortNet review showed that in the year 2010 Finnish ports handled approximately 3.3 million tonnes of liquid bulk chemicals including about 60 different chemicals. There were 7 chemicals handled more than 100,000 tonnes and 36 chemicals handled more than 10,000 tonnes. The most handled chemicals were methanol, sodium hydroxide solution and pentanes. The export of liquid bulk chemicals accounted for about 71 % and import of liquid bulk chemicals about 29 % of all liquid bulk chemicals handled in Finnish ports in the year 2010. Based on PortNet review, the most exported liquid bulk chemicals through Finnish ports were methanol, pentanes and xylenes while the most imported liquid bulk chemicals were sodium hydroxide solution, ethanol and ethanol solutions, and propane. When compared to the year 2008, the total volume of liquid bulk chemicals handled in Finnish ports in the year 2010 has decreased approximately 5 %. The number of different liquid bulk chemicals has also decreased from about 80 to 60. However, the most handled liquid bulk chemicals has remained quite the same in Finnish ports during these years.

Road and rail transport of chemicals in Finland in the year 2007 accounted for 15.1 million tonnes, in which the share of road transport was 9.5 million tonnes (62 %) and the share of rail transport 5.6 million tonnes (Häkkinen, 2009). However, it should be noted that the exact amounts of chemical transport on Finnish roads are poorly known. That is why the scoring was based mainly on ports chemical handling data obtained from Portnet. The possible data gaps were filled from information obtained from Uljas database of Finnish Customs, and directly from the companies regarding the use and land transportation of chemicals in the year 2008. As a result, the transport volume classes used in risk assessment are presented in Table 1.

3.2. Survey of past chemical accidents

Maritime

Past incidents/accidents are, when reported in detail, first hand sources of information on what may happen again (Mamaca *et al.*, 2009). However, the quality of the information dictates its usefulness, and concerning the Baltic Sea, the most important accident studies includes Rytkönen and Hänninen (2006), Molitor (2006), Mullai (2007), Suominen and Suhonen (2007) and EMSA (2010). European Maritime Safety Agency (EMSA) states that 75 ships navigating in the Baltic Sea were involved in accidents during the year 2009. These include sinkings (3 accidents), groundings (33), collisions (24), fires and explosions (10) and other types of accidents (5) (EMSA, 2010). However, HELCOM reports as many as 105 accidents in year the 2009. Ten of these accidents resulted in sea and shore pollution, but in all of the cases the cargo in question was oil. During the previous five years, there have been 628 accidents, of which 41 resulted in pollution. However, only in one case the polluting substance was reported to be a chemical, as in 2007 potassium chloride was released into the sea. In all the other cases the polluting substance was categorized as oil or unidentified (Luhtala, 2010).

Mamaca *et al.* (2009) established a clear view of lessons learnt by surveying the 47 best-documented maritime transport accidents in the World. They stated that the quality of incident reports and their accessibility are usually far from good. Mullai (2007) surveyed in his thesis altogether 22 hazardous accidents and incident databases and concluded that only the U.S. databases gave thorough information about chemical transportation incidents (inc. accident, small spills etc.) and that the best database is the U.S. HMIS (Hazardous Materials Incident System). General statistics showed that altogether 592 accident or incidents in water transportation of hazardous materials occurred in United States during the years 2002–2011 and that the annual range was between 10 and 105 incidents. Interestingly in the year 2011, more incidents in water transportation happened in transit (50 incidents) than e.g. during unloading (5 incidents). In rail/road transportation the opposite is true.

The HASREP project listed the major chemical incidents (above 70 tonnes) at sea in the European Union maritime over a period of 10 years (1995–2004). The average occurrence for the 1995–2004 decade was nearly 2 incidents per year (HASREP, 2005). By comparison, the statistical study made by the U.S. Coast Guard (USCG) in the United States over 5 years (1992–1996) listed 423 spills of hazardous substances from ships or port installations, giving an average of 85 spills each year. The 9 most frequently spilled products were sulfuric acid, phosphoric acid, caustic soda, acrylonitrile, vinyl acetate, benzene, toluene, xylene and styrene. Over half of the spills were from ships (mainly carrier barges) and the rest from facilities (when the spill comes from the facility itself or from a ship in dock). A complementary study made over a period of 13 years (1981–1994) on the 10 most important port zones reports 288 spills of hazardous substances, representing 22 incidents each year (USGC, 1999). Small spillages in Europe are not recorded with the same care, because they are not detected and/or there is a lack of communication between environmental organizations and competent authorities (HASREP, 2005).

Road/rail

Accidents which occur while transporting dangerous goods are rare when compared to the transport volumes. For example, there have only been 8 chemical transportation accidents in Finland per 1.1 billion ton kilometers (Häkkinen, 2003). The probability of a transport accident involving hazardous materials in Sweden was calculated to be 0–0.6 accidents per year per 10 million kilometres. Similarly in Norway, the probability was 0.12 accidents per a million kilometres based on the 1990–1994 data (FARGO, 2000). Finland´s Pronto database in the period of 2003–2008 contained only 35 accidents involving hazardous materials, 6 of which occurred during transport (Pronto, 2009).

Accidents involving chemicals or hazardous materials occur more often on roads than on railways. This could clearly be seen from the data acquired from the U.S. HMIS database. In the year 2011, there were 11,913 road transportation accidents and 694 railway accidents, i.e. the difference is 17-fold (HMIS, 2012). The trend was also similar in the study of Oggero *et al*. (2006) that was based on the MHIDAS database: 63 % of accidents occurred on roads and 37 % on railways. In Finland, the overall probability of an accident occurring on railways is clearly lower than that on roads. Rail transport is on average 14 times safer than road transport. Further, if looking at deaths caused by accidents, train transportation is up to 30 times safer a mode of transport than the road (Arposalo and Liedes, 2007). However, these results are not directly linked to the transport of hazardous materials.

Accident probability increases substantially in dense traffic areas. Oggero *et al*. (2006) revealed that a vast majority of the accidents that they examined occurred on motorways (81.4 %), while 7.6 % of the accidents occurred on smaller roads and crossings. Only 3.3 % of the accidents happened in tunnels, but these incidents were often severe and difficult for rescue services. Accidents involving hazardous materials more often happen during other activities than transportation. Many databases demonstrate that more incidents occur during unloading/loading than in transit phase (e.g. HMIS, 2012; CANUTEC, 2008). However, based on the U.S. HMIS database, the cost of the incident was much higher if it happened in transit phase (Table 2). This is because in the terminal/port operations precaution measures have been taken and rescue plans have been made to prevent damages to the environment. It is more difficult to take proper precautionary measures outside the closed terminal area and, therefore, the risk of polluting the environment and clean-up costs are higher in accident situations outside the warehouse area. The scenarios which caused the greatest environmental disasters occurred when a chemical transported in liquid form was involved in an accident and rapidly absorbed into the soil or spread to nearby water bodies or groundwater (Anderson, 2005; HMIS, 2012).

Table 2. Road incidents in year 2011 including hazardous materials and their costs by transportation phase (HMIS, 2012).

Transportation phase	Incidents	Hospitalized	Non-hospitalized	Fatalities	Damages
In transit	2,507	6	34	9	$78,727,757
In transit storage	301	0	4	0	$122,357
Loading	2,204	0	21	1	$780,719
Unloading	6,784	9	35	0	$16,918,296
All together	11,796	15	94	10	$96,549,129

Both from a Finnish and a global perspective, fuels and corrosive chemicals are transported the most (Häkkinen, 2003; Häkkinen 2009). The greatest accident risks are posed by the chemicals that are transported the most i.e. liquid fuels. This was apparent from almost all of the data sources used. The HMIS database also showed that the accident figures have not changed significantly in ten years (HMIS, 2012). By far the most serious accidents occurred during the transportation of liquid fuels and for instance, in the ASHMIR database, two-thirds of all accidents related to fuel liquids (Winder *et al*. 2001). A lot of incidents also occurred when acidic and alkaline substances were transported. An interesting exception to this observation could be found in a Canadian data source based on the CANUTEC statistics for the years 1990–2007. This data showed, in turn, that more accidents occurred while transporting corrosive materials than fuels (CANUTEC, 2008).

Chemical accidents most often occur when a truck tank or a rail car carriage is damaged and a fairly small spill leaks onto the soil. Based on the MHIDAS database, a leakage/spill/emission was the most common type of accident during transport (78% of cases), followed by fire (28 %), explosion (14 %) and a cloud of gas (6 %) (Oggero *et al*. 2006). The gross margin in Oggero`s study was over 100 % since some accidents could be classified into more than one category. When looking at the incident chains, it could be observed that in the majority (62 %) of accidental spillage cases, no additional risks existed (Oggero *et al*. 2006). In turn, according to the ARIA database on all industrial accidents (incl. transport), the most common types of accidents involved fires (51 %) and hazardous substance spills/discharges (47 %) (Technological Accidents Report 1992–2005).

Only a few reports can be found on the environmental impacts of transport-related accidents involving hazardous materials. Based on different databases and studies it appears that damage to the environment happens rarely, but this result can be very misleading. In the MHIDAS database, there were only 21 transport-related chemical accidents that caused harm to the environment (Vince, 2008). Similarly, in the HMIS database in the year 2011, there were only 63 reported accidents that resulted in environmental damage, when the total number of accidents recorded in the database was over 14 000 at that time period (Table 3). It is also significant to notice that since environmental damages were reported very seldom, the damage costs of those few cases that were reported have been remarkably high. Most of the environmentally harmful accidents were spills and are included to the spills and leaks category in this cost analysis.

Table 3. Consequences of incidents/accidents (all transport modes) including hazardous materials in United States in year 2011 (HMIS, 2012).

Result	Incidents	Hospitalized	Non-hospitalized	Fatalities	Damages
Environmental damage	63	1	5	5	$35,786,175
Explosion	12	3	3	7	$6,062,429
Fire	61	10	14	10	$14,949,510
Material entered waterway/sewer	47	0	6	4	$26,875,837
None	745	1	0	0	$1,552,128
Spillage	12,732	13	109	7	$94,711,105
Vapor (Gas) dispersion	436	9	31	3	$18,706,850

The results of many sources show that more chemical accidents occur during transport on roads than on railways, but assessing the risks pertaining to this is not as clear cut. Databases such as the MHIDAS include many worst case scenario examples of railway transportation risks and problems, when for instance several rail cars full of various chemicals are involved in an accident (Vince, 2008). In these cases, the hazard potential to the environment and health is much greater than in road accidents.

3.3. The priority list

The chemicals with the highest score in the priority list (Table 4) can be considered to be the ones with the greatest environmental risk. In the case of marine accident, the greatest risk to the environment is posed by chemicals which have high solubility, stay in the water column, and are bioavailable, persistent and toxic to organisms. Nonylphenol is the most toxic of the studied chemicals and it is also the most hazardous in case of maritime spills. It is persistent and accumulative and has relatively high solubility to water. Nonylphenol is actually transported in the form of nonylphenol ethoxylates but it is present as nonylphenol when spilled to the environment and in this study the worst case scenario was evaluated. Other very hazardous substances were sulphuric acid and ammonia (Table 4). The HASREP (2005) project identified top 100 chemicals transported between major European ports and involved trade through the English Channel to the rest of the World. The assessment was based on both transport volumes and the GESAMP hazard profile. They highlighted chemicals like benzene, styrene, vegetable oil, xylene, methanol, sulphuric acid, phenol, vinyl acetate, and acrylonitrile. They concluded that these chemicals were the ones that have high spillage probability but may not result in significant environmental impact. Similarly, French McKay *et al*. (2006) applying a predictive modeling approach for a selected range of chemicals that are transported by sea in bulk concluded that phenol and formaldehyde present the greatest risk to aquatic biota. Furthermore, Guerbet and Jouany (2002) evaluated 90 chemicals using the SIRIS method according to the risk that they pose to the aquatic environment. Only a few chemicals included in our study were present in study of Guerbet and Jouany (2002), but e.g. benzene was ranked 6th (high risk for the environment), chloroform as 14th while e.g xylenes was ranked number 88th. Harold *et al*. (2011) evaluated human health risks of transported chemicals based on the GESAMP ratings for toxicity and irritancy. This gives more weight to chemicals that are floaters, form gas clouds, irritate and are toxic like chlorine (Harold *et al*. 2011). It is clear that different weightings have a certain impact on the difference in results in these studies. In this paper, the effects to water column biota as well as accident probability were weighted.

In the case of an on-land accident, the greatest threat to the environment is the transport of a toxic, persistent and accumulative chemical into ground water and further to water intake areas as well as the uncontrollable spreading of the chemical into the surrounding environment. If the chemical spreads into areas which are out of the rescue service's reach, the costs of remediating the site increase greatly. Nonylphenol was ranked the most hazardous chemical in soil (as well as in sea) due to its toxicity, long persistency in the environment and high accumulation potential. However, nonylphenol does not transport easily into soil which aids in its remediation in accident situations. The next most hazardous chemicals are phenol, ammonia and sulphuric acid (Table 4). The effects that ammonia and sulphuric acid have on the environment can be very complex, since for instance pH, temperature and precipitation conditions have a great impact on their environmental fate. In accident situations, ammonia vaporizes easily, forming a toxic gas cloud. In water, it is extremely toxic to water organisms. Sulphuric acid is very reactive and corrosive. Its toxicity is based on the powerful oxidation potential of the hydrogen ions – the toxicity of sulphuric acid applies for all other acids. Its impact on organisms depends on the ecosystem´s intrinsic pH and buffering capacity. Sulphuric acid also releases attached metal ions in soil and sediment, thus increasing their transport and bioavailability to organisms. Jeong and An (2011) ranked soil pollution substances with the CROSS scoring method. Metals were ranked as the most hazardous soil pollutants but in the list of 56 substances, the rank order was 7, 14, 16, and 24 for phenol, benzene, toluene and MTBE. The placements are in good accordance with the results of this study, but some differences in the order of chemicals exist because of different weightings.

The scoring method and parameters used in this study have both similarities and differences when compared to other scoring systems. Chemicals are scored from environmental hazard´s point of view, in systems such as, ERICA (Boriani *et al.*, 2010), CROSS (Jeong and An 2011), PestScreen (Juraske *et al.*, 2007), EURAM (Hansen *et al.*, 1999) and CHEMS-1 (Swanson *et al.*, 1997). Most of these methods rely on calculating the Predicted Environmental Concentration (PEC), creating models of the environment with the use of monitoring data. However, the PEC/PNEC (Predicted Non-Effective Concentration) method has not developed for the on land accidental situation, but for measuring the long-term exposure from distributed sources. Assessing the behaviour and transport of chemicals in soil is challenging although many comprehensive numerical models such as STOMP and simpler screening models like HSSM and HMTECM have been developed for assessing chemical migration in different phases in soil as a consequence of an accidental spill (Yoon *et al.*, 2009). However, the PEC/PNEC ratio may be a suitable tool for the evaluation of aquatic exposure and effects. However, in this study, PEC was not determined for maritime accident since it demands complex 3D modeling with e.g. the CHEMMAP program (French McKay *et al.*, 2006) and this is beyond the scope of the Chembaltic project.

CHEMS-1 (Swanson *et al.*, 1997) had very similar parameters as were used in our scoring method including toxicity values, persistence, bioaccumulation, degradation and amount of release. In their Environmental Consequence Index (ECI), Arunraj and Maiti (2009) had a different approach and focused on the environmental fate and distribution of chemicals as did Davis *et al.* (1994) with a different parameter set. The combination of these three forms the basis of the ChemRisk scoring method (Häkkinen *et al.* 2010) used in this study. Equal to CHEMS-1, our scoring applies to calculated/measured values removing the subjectivity that could occur if scores were assigned simply on the basis of expert opinion. In both scoring systems, the combination of scores from the release and exposure data gives the final score transparency and clearly indicates the significance of risk. In cases where no experimental data is available, the predicted/modelled values are used. However, CHEMS-1 uses a two-tiered approach that significantly reduces the number of chemicals that need detailed evaluation (Swanson *et al*. 2007). On the other hand, the EURAM method (Hansen *et al*. 1999) having separate scores for human health and environment had similarities to our scoring method, but human risks are weighted more in EURAM method.

Table 4. Chemical scores of different parameters, the sum total of given points and placement in the priority list. The chemicals with the most points pose the greatest environmental risk.

Chemical	Soil only		Sea only									Soil list		Sea list	
	Density/viscosity	Adsorption	Water solubility	Density	Volatility	Biodegradability	Accumulation	Acute toxicity	Chronic toxicity	Transport volume	Other hazardous impacts	Total sum	Placement	Total sum	Placement
Nonylphenol	1	1	1	2	2	3	3	3	3	2	1	19	1	20	1
Sulphuric acid	2	3	3	2	3	2	1	2	2.5	2	0	17.5	3	17.5	2
Creosote	2	1	2	2	2	3	2	2.3	2.3	1	0.5	16.1	7	17.1	3
Phenol	3	3	3	2	2	2	1	2	2	3	0	18	2	17	4
Ammonia	2	3	3	1	1	2	1	3	2.5	2	1	17.5	3	16.5	5
Bronopol	3	3	3	2	3	2	1	2.3	2	1	0	17.3	5	16.3	6
Benzene	3	2	3	1	1	3	1	2	1.5	2	0.5	16	8	15	7
Glutaraldehyde	2	2	3	2	2	2	1	2.7	1.3	1	0	14	23	15	7
Styrene	3	1	2	1	1	2	2	2.3	2.5	2	0	15.8	10	14.8	9
Chloroform	3	3	3	2	1	3	1	2	1	1	0.5	15.5	11	14.5	10
Xylenes	3	2	2	1	1	2	2	2	1.3	3	0	16.3	6	14.3	11
Divinyl benzene	3	1	2	1	2	2	2	2.3	2	1	0	15.3	12	14.3	11
Sodium chlorate	3	3	3	2	3	2	1	1	1.3	1	0	15.3	12	14.3	11
Resorcinol	0	3	3	2	2	2	1	2	1.3	1	0	12.3	29	14.3	11
Ethylene dichloride	3	3	3	2	1	3	1	1.7	1	1	0.5	15.2	14	14.2	15
MTBE	3	3	3	1	1	2	1	1	1	3	1	16	8	14	16
Epichlorohydrin	3	3	3	2	1	2	1	2	1.5	1	0.5	15	15	14	16
HCFC	3	3	3	2	1	3	1	2	1	1	0	15	15	14	16
Carbon disulphide	3	3	3	2	1	2	1	2	1	1	0.5	14.5	20	13.5	19
Toluene	3	2	2	1	1	2	2	2	2	1	0	15	15	13	20
Acrylonitrile	3	3	3	1	1	2	1	2	1.5	1	0.5	15	15	13	20
n-Pentane	3	2	2	1	1	1	2	2	1	3	0	15	15	13	20
Methanol	3	3	3	1	1	1	1	1.3	1	3	0	14.3	21	12.3	23
TDI	3	1	1	2	2	1	2	1.7	1	1	0.5	13.2	28	12.2	24
Ethanol	3	3	3	1	1	1	1	1	1	3	0	14	23	12	25
ETBE	3	3	3	1	1	2	1	1	1	2	0	14	23	12	25
Methyl methacrylate	3	3	3	1	1	2	1	1.7	1	1	0	13.7	27	11.7	27
1-Decene	3	2	1	1	1	2	3	1.3	1	1	0	14.3	21	11.3	28
1-Hexene	3	3	2	1	1	1	2	2	1	1	0	14	23	11	29
NexBTL	2	1	1	1	1	1	3	1	1	2	0	12	30	11	29

The UN group of experts on scientific aspects of marine environmental protection (GESAMP) has established a process for the evaluation of the hazards of harmful substances carried by ships (GESAMP, 2002). The GESAMP hazard profile is a comprehensive risk evaluation of chemicals transported in marine environment (GESAMP, 2002) and we are not trying to improve or replace that. However, in this study, more weight is given to the ecological effect of most transported chemicals for water column biota and less to theirs human health effect than in the categorization of GESAMP. In our scoring system the most harmful chemicals are those that are very water-soluble, persistent, bioavailable and have high acute and chronic toxicity. Based on the GESAMP evaluation IMO has formed 4 different hazard categories X (major hazard), Y (hazard) and Z (minor hazard) and other substances (no hazard) (IMO, 2007). Although this approach of categorizing the chemicals into different categories gives a cohesive and easy means of measure the danger posed by an individual chemical, it does not, however, give the complete information: are all chemicals within the same category equally damaging from an environmental perspective? Almost all chemicals studied in this paper belong to category Y, and still their environmental hazard potential and e.g. toxicity mechanisms may be significantly different.

4. CONCLUDING DISCUSSION

In terms of risk management, the past accident data can help to avoid a similar accident happening again. For this study, especially rail or road chemical accidents were studied by utilizing several databases. Although the data concerning the environmental effects of accidents were very incomplete, certain regularities were easy to detect, such as the fact that most accidents happen with chemicals that are transported to the most. In addition, the frequency of the road accidents was higher than that of rail or water transport. Potential quantities of a chemical transported per trip are, however, much higher in the latter ones, which increases transport-related risk in these modes. In the case of road/rail transportation of dangerous chemicals, the costs of the accident are the greatest in the transit phase even if more accidents happen in the loading and unloading phase. Interestingly, in shipping most accidents occurred in the transit phase (HMIS, 2012).

Data about the chemical transportation accidents in Finland and in the EU are limited and decentralized. With some exceptions (e.g. U.S. HMIS), chemical accident databases worldwide, at their best, only provide information on the accident types that could cause damage to the environment. Monitoring newspaper articles on accident situations often leads to the feeling that not all dangerous chemical accidents end up in the official databases of Finland or the EU, either due to a delay or the databases´ classification system. The need for a common relational model database for all authority parties is apparent. Except for Finland and Sweden, the exact quantities of different chemicals transported are also unknown in the Baltic Sea. It would also be essential to pay attention to what chemicals are transported by land and in what quantities. At the moment, information seems to be scattered in different companies, ports and agencies and classified as confidential. The environmental and rescue authorities should be kept well informed on the transport of dangerous chemicals since this would make preparing for accidents and the rescue services overall a lot easier to manage and arrange.

A priority list of the regionally most transported chemicals for both marine and rail/road accident situation was formed in this study. The method used has many similarities with other commonly used scoring systems but this study gave more weight to specific characteristics of accidental release, the Baltic Sea region and impact on the environment. Nonylphenol, ammonia, sulphuric acid, phenol and creosote were ranked the most hazardous substances.

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